



Carbon nanotube-coated stainless steel mesh for enhanced oxygen reduction in biocathode microbial fuel cells



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HIGHLIGHTS

- CNT-coated stainless steel mesh (CNT-SSM) was fabricated by a simple, scalable process.
- The CNT-SSM showed a three-dimensional network structure.
- The CNT-SSM biocathode performed better catalytic activity toward oxygen reduction.
- The electrochemical capability of cathodic biofilms was characterized by CV.
- The CNT-SSM biocathode can meet the required shape for different MFC application systems.

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ABSTRACT

A novel carbon nanotubes (CNTs) coated stainless steel mesh (SSM) electrode has been fabricated by a simple and scalable process and is used as biocathode in microbial fuel cell (MFC) for performance improvement. Examination by scanning electron microscope shows that CNTs are uniformly distributed over the surface of the SSM, thus forming a three-dimensional network structure. The MFC with CNT-SSM biocathode achieves higher maximum power density (147 mW m^{-2}), which is 49 times larger than that (3 mW m^{-2}) produced from the MFC with bare SSM biocathode. Moreover, cyclic voltammetry shows that the microorganisms on the CNTs-SSM biocathode play a major role in oxygen reduction reaction (ORR), and the CNT-SSM biocathode performs better catalytic activity toward ORR than that of SSM biocathode. Additionally, the MFC with CNTs-SSM biocathode has higher Coulombic Efficiency than that of MFC with bare SSM biocathode. In this study, we demonstrate that the use of CNTs-SSM offers an effective mean to enhance the electricity of biocathode MFCs.

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1. Introduction

Microbial fuel cells (MFCs) utilize microorganisms as catalysts, which can decompose organic or inorganic matter and simultaneously harvest electricity [1]. Initially, workers generally used chemical cathode system in MFCs, such as coatings of the noble metal platinum (Pt), transition metal macrocycles [2], and phthalocyanines [3] to catalyze the oxygen reaction. These catalysts, however, are often expensive, and/or unsustainable, which is

detrimental to further scale up in wastewater treatment scenarios. Recently, biocathode has drawn considerable attention due to its several advantages over the chemical cathode, e.g., lower cost, sustainability and functions for wastewater and biosynthesis [4,5]. In a biocathode MFC, oxygen from open air can be effectively reduced by accepting electrons from cathode electrode via the catalysis of electrochemically active microorganisms, resulting in significantly improved cathode performance [6]. He and Angenent extensively reviewed several possible biological cathodic processes, such as the reduction of oxygen, nitrate and sulfate [7].

Cathode materials and their spatial orientation significantly affect biocathode performance [5], since they play a crucial role in the oxygen reduction, the biofilm formation, and the microbial process. Thus, identification of cathode materials that maximize microbial activity for oxygen reduction is within the main challenges in construction of a biocathode MFC. Consideration of

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selecting biocathode material should focus on high-quality of conduction, mechanical strength, chemical stability, and biocompatibility [4]. To date, a variety of carbon-based materials including carbon paper [8], carbon cloth [9], graphite fiber brush [10], have been evaluated as biocathodes in MFCs. Unfortunately, the high cost of some of these materials, such as carbon cloth (ca. \$1000 m⁻¹), prohibits the use of this material for large scale systems. While stainless steel mesh (SSM), widely used in corrosive environments, has been investigated as biocathodes in MFCs due to its low cost and durability. De Schampheleire et al. [11] reported that a SSM used as biocathode obtained a power density of 20 mW m⁻² in freshwater MFCs, but was lower than carbon felt. In another study under a polarized of -0.6 V vs Ag/AgCl, SSM performed better than graphite in supporting biocathode in sediment MFC when the reactor was inoculated with *Geobacter sulfurreducens* [12]. Recently, Wang et al. demonstrated that oxygen reduction reactions were effectively catalyzed by the microorganisms attached on the SSM, and a power density of 4.35 W m⁻³ was achieved.

Over the years, considerable efforts were made to enhance the anodic electron transfer by modifying the surface of anodes [13]. Potentially, modification of biocathodes surface is also expected to optimize the extracellular electron transfer on the biocathode in MFCs. Thus far, few studies are reported on the biocathode material fabrication toward oxygen reduction, especially by employing nanostructured materials. Zhuang et al. [9] reported that the maximum power density achieved by using graphene-modified carbon cloth could be 2 times higher than that achieved with bare carbon cloth. Carbon nanotubes (CNTs), as a new class of carbon nanomaterials, have been evaluated as possible anode, chemical cathode and biocathode materials in MFCs due to its unique properties materials such as higher active surface area, excellent conductivity, tailored nanostructure to adsorb bacteria. Recently, Liu et al. [8] fabricated a biocathode by electrodepositing CNTs and chitosan onto a carbon paper for oxygen reduction, and the use of this conductive and compatible CNT/chitosan nanocomposite achieved superior performance compared to the control. However, the electrodepositing strategy mentioned above is current consuming and usually bring in other chemicals (use of binders), which is not conducive to the economical production of MFC biocathodes. In addition, the carbon paper used as electrode substrate in above study is brittle and not cost-effective. Therefore, modification strategy needs further improvement and seeking a preferable electrode substrate is warranted.

In this study, we changed the electrode substrate from carbon paper to SSM, and fabricated a homogeneous and stable CNT-SSM biocathode through a simple and scalable process: dipping–drying of a piece of SSM in aqueous CNT ink. We also presented the investigation of MFCs with CNT-SSM or control used as biocathode for oxygen reduction based on aerobic microorganisms as catalysts. Performance of these biocathode MFCs were compared and evaluated via current density, power density, and polarization curves. Moreover, the electrochemical capability of cathodic biofilms was characterized by cyclic voltammetry (CV). The use of durable metallic backbones combined with CNTs could offer exciting opportunities in the advancement of MFC biocathode design and applications.

2. Materials and methods

2.1. CNT-SSM electrode synthesis

Carbon nanotubes (CNTs, diameter of 40–60 nm, Shenzhen Nanotech Port Co., Ltd.) were ultrasonically dispersed in a mixture of H₂SO₄–HNO₃ (volume ratio: 3:1) for 5 h then filtered through a polytetrafluoroethylene filter membrane (pore diameter 0.4 μm)

and washed with de-ionized water until the slurry with pH 6–7 was obtained. Aqueous CNT ink was prepared by dispersing the carboxylated CNTs in de-ionized water with sodium dodecylbenzene sulfonate (SDBS) as a surfactant. The dispersion was ultrasonicated for 1 h to obtain a homogeneous solution. The concentration was 0.18% for CNTs and 1% for SDBS by weight. A piece of SSM (thickness of 100 μm, diameter of 50 μm, Anping Count Resen Screen Co., Ltd. China), with a projected surface area of 7 cm², was then dipped into the CNT ink, removed and dried at 100 °C to obtain a CNTs-modified electrode. The dipping–drying process was repeated for 3 times to increase the CNTs loading in SSM.

2.2. MFC construction and operation

The volume of anodic chamber was 40 mL (2 cm in length and 5 cm in diameter) with a net volume (liquid volume) of 30 mL. During the MFC start-up stage, the carbon paper (thickness of 0.35 mm, diameter of 10 μm, Shanghai Hesen Co., Ltd.) coated with Pt of 0.5 mg cm⁻² (Shanghai Hesen Co., Ltd.) was used as the cathode. The coated side of the cathode was positioned facing the cation exchange membrane (CEM, Zhejiang Qianqiu Group Co., Ltd.), with the uncoated side directly exposed to air. Graphite felt (thickness of 5 mm, diameter of 15 μm, Beijing Sanye Co., Ltd.) with a projected surface area of 7 cm² was used as the anode and was placed in the chamber at a distance of 0.5 cm from the cathode. The single-chamber MFC were inoculated with anaerobic sludge (obtained from Liede Sewage treatment plant, Guangzhou, China) and a medium containing sodium acetate (1000 mg L⁻¹), a phosphate buffer solution (PBS, 100 mM), minerals (12.5 mL L⁻¹), and vitamin solution (12.5 mL L⁻¹) as described in our previous study [14].

After the output voltage was stabilized at 350 mV (with a fixed external resistance of 1 KΩ), the single-chamber MFC was changed and operated in a dual-chamber model. The cathodic chamber was of the same shape and size to the anodic chamber. A CNT-SSM and a bare SSM (for comparison) electrode, with a projected surface area of 7 cm², was used as biocathode, respectively. The bio-cathodic chamber inoculation was the same as the anodic chamber and was fed with the same medium, but without sodium acetate. The cathodic chamber was continuously saturated with air as a cathodic electron acceptor with an air pump. The anode solution was refreshed when the voltage dropped below 20 mV. All MFCs were operated in fed-batch mode at 30 ± 1 °C in a temperature-controlled room.

2.3. Analysis and calculation

The output voltage across a 1 KΩ external resistor was automatically recorded every 5 min using a data acquisition system (Model 2700, Keithly Instruments, USA). Polarization curves were obtained by varying the external resistance (R_{ex}) over a range from 50 to 8000 Ω as the voltage output achieved a steady state. Current density (A m⁻²) was calculated as $I = U/(R_{ex}A)$, and power density (mW m⁻²) was calculated according to $P = 1000 UI/A$, where I (A) is the current, U (V) is the voltage, and A (m²) is the projected cathode surface area.

The soluble chemical oxygen demands (COD) were measured according to standard methods [15] and the COD removal efficiency (δ COD) was calculated as δ COD = (COD_{int} – COD_{out})/COD_{int} × 100%, where COD_{int} denotes the initial COD concentration (mg L⁻¹) in the feed and COD_{out} stands for COD concentration at the end of the batch test. The Coulombic Efficiency (CE) was obtained as CE (%) = C_p/C_T × 100%, where C_p is the total Coulombs calculated by integrating the current over time, and C_T is the theoretical amount

of coulombs based on COD removal by assuming 4 mol of electrons per mol of COD.

Electrochemical analysis of cathodic biofilms of the bio-cathode in MFCs was conducted by cyclic voltammetry (CV), which was performed using an electrochemical workstation (Model 2273, Princeton Applied Research) with a three-electrode test system consisting of a working electrode (the bio-cathode), a saturated calomel electrode (SCE, +0.242 V vs standard hydrogen electrode, SHE) reference electrode, and a counter electrode (the anode). CV tests were conducted under open circuit voltage (OCV) condition and the voltage was changed from -0.6 V to 0.3 V in forward and reverse scans at a scan rate of 25 mV s^{-1} .

The surface morphologies of the CNT-SSM and bare SSM electrodes were observed by a scanning electron microscope (SEM) (XL-30, Philips Holland).

3. Results and discussion

3.1. Morphological characterization of CNT-SSM

A bare SSM was coated with CNTs through a simple and scalable dipping and drying process [16]. As shown in Fig. 1A, the bare SSM consists of a number of metal fibers with diameter of about $50 \mu\text{m}$. The uncoated metal fibers feature a relatively smooth surface (Fig. 1B). In contrast, the surface of the CNTs coated-SSM is much rougher (Fig. 1C and D), and hence its surface area is significantly larger. Specially, CNTs were uniformly distributed over the surface of the SSM, thus forming a three-dimensional network structure. Additionally, the coated CNTs could not be removed even under intensive sonication, indicating that the interaction between the

CNTs and the SSM was very stable. This three-dimensional nano-structure was expected to provide favorable conditions for biofilm formation. As an electrode in MFCs, CNT-SSM has the same benefits as CNT-carbon paper, including an open macroporous structure for oxygen transport and a microporous CNT layer for electrode–bio-film interaction [8].

3.2. Power output and polarization

Stable voltage (350 mV , $1 \text{ k}\Omega$) produced from the MFCs with Pt cathodic catalyst was observed in several consecutive cycles, suggesting that electrochemically active biofilm had been fully developed on anode. The MFC was then transferred to a dual-chamber mode and the anaerobic sludge was inoculated into the cathode chamber. Following inoculation, current output was generated for both MFCs as shown in Fig. 2A. During the first three cycles, the current density of the MFC with CNT-SSM biocathode increased significantly and stabilized at about 350 mA m^{-2} from the third cycle. While a much lower current density of $\sim 30 \text{ mA m}^{-2}$ was obtained in the MFC with bare SSM biocathode and the current density was barely growing for a long time. These results indicate that CNT-SSM could effectively collect electrochemically active bacterium, but bare SSM did not.

After about 50 days stable operation, the power density and polarization curves as a function of current density for the MFCs are shown in Fig. 2B and C, respectively. The maximum power density achieved by the MFC with CNT-SSM biocathode was 147 mW m^{-2} at the current density of 836 mA m^{-2} , which is 49 times larger than that (3 mW m^{-2}) produced from the MFC with bare SSM biocathode. The polarization curves in Fig. 2C showed that the anode

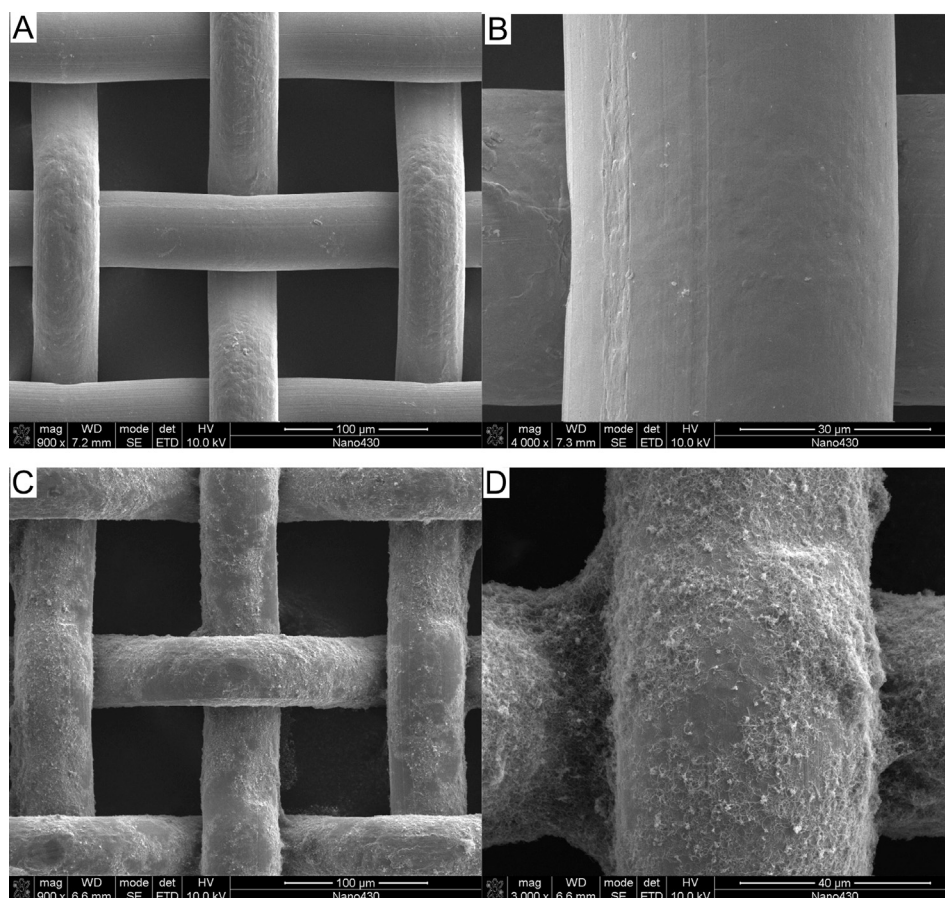


Fig. 1. SEM images of abiotic biocathodes from (A, B) bare stainless steel mesh, (C, D) CNTs-coated stainless steel mesh.

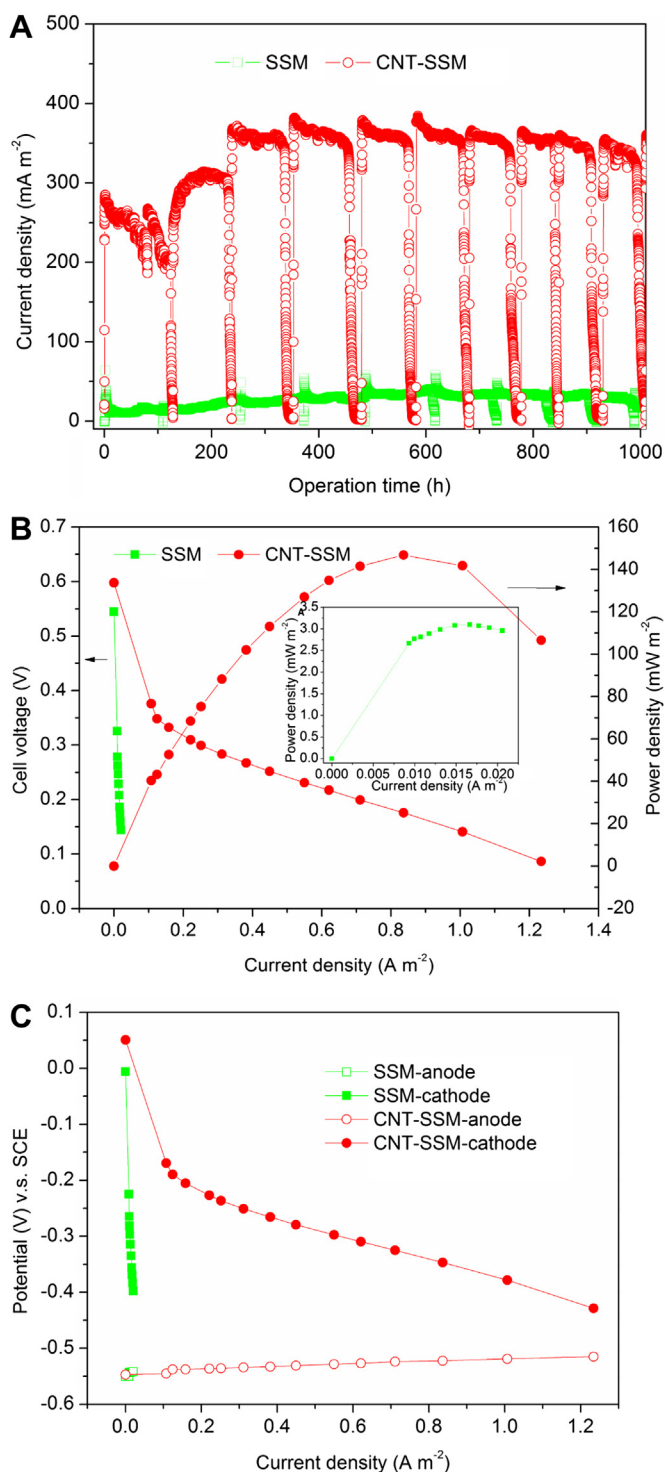


Fig. 2. Performance of MFC equipped with stainless steel mesh (SSM) and CNTs-SSM as biocathode: (A) current density as a function of time, (B) power density and cell polarization curves, and (C) anode and cathode polarization curves.

potential was not appreciably affected by biocathode, and the difference in biocathode potential, such as the open circuit potential (OCP) and slope of the biocathode polarization curve, was consistent with the orders in power density of the MFCs with both cathode materials. For instance, the OCP of CNT-SSM biocathode was 51 mV (vs SCE), which was a higher than that of bare SSM biocathode (−6 mV vs SCE). The electrochemical reaction rates in a fuel cell can

be evaluated by its OCP. A higher OCP value is related to higher reaction rate [17]. Thus, this suggests the better oxygen reduction of CNT-SSM biocathode as compared to bare SSM biocathode. In addition, the slope of bare SSM biocathode polarization curve showed a more rapid decrease as compared to that of CNT-SSM biocathode. As a result, the difference in performance of the MFCs can be attributed to the difference in biocathode performance. It is clear that CNT-SSM used as biocathode performed better than bare SSM, which was probably due to better growth of electrode-oxidizing bacterium on CNT-SS biocathode. These results indicate that the CNTs modification on SSM electrode enhanced the biofilm-driven catalysis of oxygen reduction effectively.

3.3. CV study

CV was carried out to evaluate the catalytic behavior of the biocathodes. As shown in Fig. 3A, no obvious redox peak was observed from both abiotic CNT-SSM and bare SSM electrodes either in air- or nitrogen-saturation solution. It should be noted that the current of abiotic CNT-SSM electrode in air-saturation solution was higher than that in nitrogen-saturation solution because of the oxygen reduction on the abiotic electrode. By comparison, the abiotic CNT-SSM electrode exhibited higher catalytic activity than the abiotic SSM electrode in air-saturation solution. In order to further investigate the biofilm-associated ORR, both the

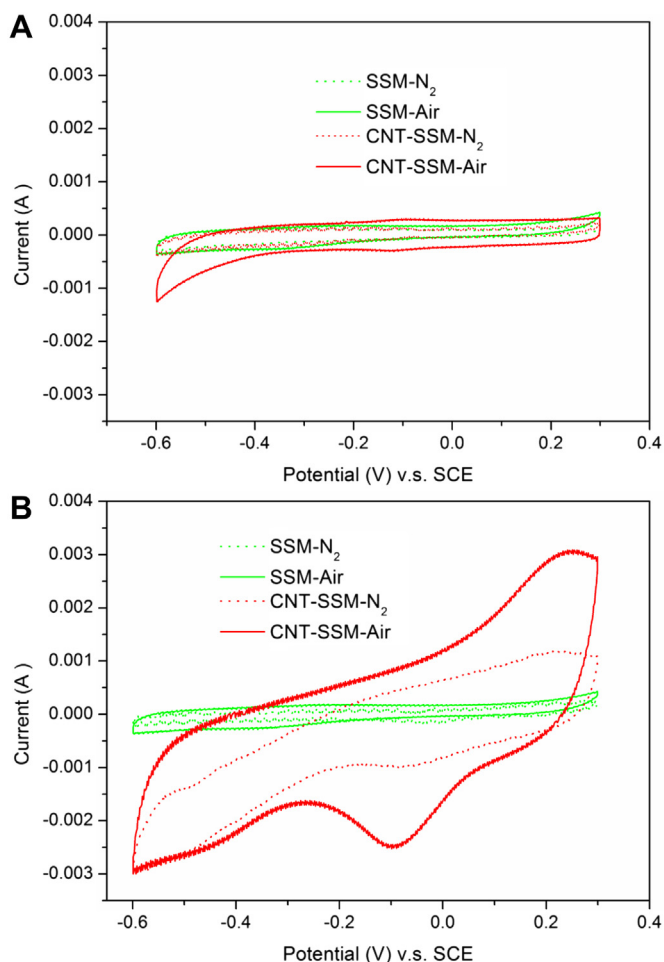


Fig. 3. Cyclic voltammetry curves for (A) raw cathode electrodes and (B) cathode electrodes with biofilm attached.

biocathodes were tested under aerobic and anaerobic conditions, respectively. As shown in Fig. 3B, for the CNT-SSM biocathodes, an obvious reduction peak was found at the potential of -0.1 V vs SCE in air-saturation solution, with a peak current 2.5 mA. However, the peak disappeared and the peak current decreased to 1 mA at -0.1 V vs SCE when the solution was purged with nitrogen, suggesting that indeed oxygen reduction was the reaction that was catalyzed. The absence of the redox peak implied a direct biofilm-mediated electrode reduction for oxygen [18]. When comparing these results with the CV of abiotic cathode in air-saturation solution (Fig. 3A), an obvious reduction peak was observed for the CNT-SSM biocathode but not for the abiotic CNT-SSM cathode, and the maximum current of the CNT-SSM biocathode was much greater than that of the abiotic CNT-SSM cathode at -0.1 V vs SCE, indicating that indeed the ORR was catalyzed by the microorganisms. In contrast, the CV of SSM biocathode in Fig. 3B showed the similar behavior and no redox wave either in air-saturation or nitrogen-saturation solution. As compared with CV of abiotic SSM cathode (Fig. 3A), the SSM biocathode also performed the same catalytic behavior in air-saturation solution, implying that the microorganism developed poorly on the SSM electrode. The results demonstrate that CNT-SSM biocathode performed better catalytic activity toward ORR than that of SSM biocathode, which was consistent with the power generation. Thus, it could be concluded that the electrochemical activity of the biofilm was promoted by CNTs. It is likely that micrometer-scale structures and three-dimensional nanostructure (CNTs modified-SSM, as revealed by SEM) facilitated the attachment of microorganisms to the CNT-SSM biocathode, thus enhancing the biofilm associated-ORR.

3.4. COD removal and CE

COD removal and CE of the MFC with CNT-SSM and SSM biocathodes were investigated during a batch-operated model, as shown in Fig. 4. The acetate removal efficiency remained at a high level for the MFCs with the two different biocathodes. 92% and 86% of COD was removed from the MFC with CNT-SSM biocathode and SSM biocathode, respectively. The CE of the CNT-SSM biocathode was 16.6%, while the CE only reached 1.6% with the SSM biocathode, and this agreed with the results of polarization and power measurements. This likely resulted from faster oxygen reduction kinetics of CNT-SSM biocathode with more developed microorganisms as catalysts, promoting quantitative conversion of

organic substrates to Coulombs. Therefore, it is likely that the better performance of biocathode benefited the growth of electricity-generating microorganisms in the anode chamber and thus resulting in increased COD removal and CE.

3.5. Significant and potential of CNT-SSM biocathode in MFCs

Biocathodic CNTs modification is a relatively new field of research and very little effort has been made on it. A prior work [8] fabricated a CNTs/chitosan biocathode by electrodepositing CNTs and chitosan onto a carbon paper, and the current density and maximum power density of the MFC increased by 67% and 130% as compared to the control. To our knowledge, the costs associated with the MFC construction should be lowered during the MFC application into wastewater treatment. In this study, we changed the electrode substrate from carbon paper (brittle and not cost-effective) to SSM and employed a simple and scalable process to directly fabricate a homogeneous and stable CNT-SSM biocathode. We showed that the CNTs-SSM biocathode enables effective oxygen reduction in the biocathode MFC, as revealed by CV test. More importantly, the use of inexpensive SSM and the simple fabricating method lowered the MFC construction costs, which is conducive to the scale-up of MFCs. The other advantage of using SSM as biocathode substrate is the uniform pore diameters and the tenability (it can be tuned during SSM synthesis) over a wide range. Therefore, improvements to the manufacturing process may further increase the efficiency of CNTs-SSM biocathode. For instance, biofilm growth on the biocathodes could be optimized by altering the pore size (conducted during manufacturing process of SSM), thus, leading to further increases in MFC power densities. Another area for further development is the shape of SSM, as it is flexible and can be bent arbitrarily to any degree. Therefore, the CNT-SSM biocathode are allowed to meet the required shape for different MFC application systems, such as cubes, cylinders [19], or strips.

4. Conclusion

CNTs-coated SSM, as a novel and inexpensive material with a three-dimensional structure, was employed as the biocathode in MFCs. The MFC with CNTs-SSM biocathode exhibited better electrochemical performance (power generation, polarization and CV performance) and higher utilization for the electricity generation (Coulombic Efficiency) than that of the MFC with bare SSM biocathode. CV tests demonstrated that CNT-SSM biocathode performed better catalytic activity toward ORR than that of SSM biocathode, thus resulting in the significantly enhance performance of MFCs. In addition, use of SSM for CNTs coating appears superior to previously studied carbon paper, graphite fiber and carbon cloth, providing a three-dimensional surface, controllable pore sizes, and tunable shape for MFC biocathodes application. The CNTs-SSM electrode therefore offers a good prospect for biocathode application in MFCs, and further studies are necessary to optimize mesh pore size for efficient biofilm associated-ORR on biocathode and to examine different shape of CNTs-SSM biocathodes during MFC application.

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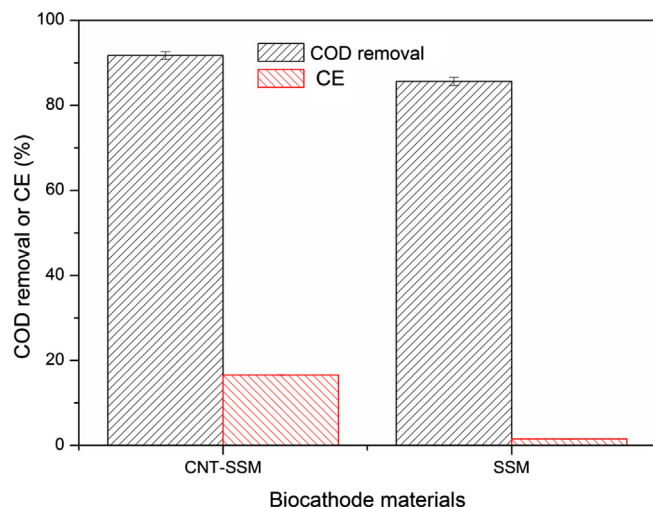


Fig. 4. COD removal and coulombic efficiency (CE) of biocathodic materials.

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